PB82-234261

Laboratory Evaluation of Commercially Available Passive Organic Personal Monitors

Battelle Columbus Labs., OH

Prepared for

Environmental Monitoring Systems Lab.
Research Triangle Park, NC

Apr 82

U.S. Department of Commerce
National Technical Information Service
NTIS

BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE
DROPPED HEAD; BEGIN SECTIONS HERE
6-1/2"
9-1/8"
BEGIN LAST LINE OF TEXT
3/8"
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
PAGE NUMBER
EPA-287 (Clin.)
(4-76)

PB82-234261

EPA 600/4-82-031
April 1982

FINAL REPORT

on

LABORATORY EVALUATION OF COMMERCIALLY AVAILABLE PASSIVE ORGANIC PERSONAL MONITORS

by

Robert W. Coutant
Battelle Columbus Laboratories
Columbus, Ohio 43201

Contract Number 68-02-2686

Project Officer

Donald R. Scott
Office of Research and Development
Environmental Monitoring Systems Laboratory
Research Triangle Park, NC 27711

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

REPRODUCED BY
NATIONAL TECHNICAL INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/4-82-031	ORD Report	PB82 234261

4. TITLE AND SUBTITLE	5. REPORT DATE
Laboratory Evaluation of Commercially Available Passive Organic Personal Monitors	April 1982
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
R. W. Coutant	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Battelle Columbus Laboratories 505 King Avenue Columbus, Ohio 43201	11. CONTRACT/GRANT NO. 68-02-2686 Task 128
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
U. S. Environmental Protection Agency Environmental Monitoring Systems Laboratory Research Triangle Park, North Carolina 27711	Final 14. SPONSORING AGENCY CODE 600/4

15. SUPPLEMENTARY NOTES

16. ABSTRACT

A laboratory investigation was conducted to determine the potential utility and limitations for the use of commercially available passive dosimeters for monitoring volatile organic compounds at ambient levels. Test compounds included chloroform, 1,2-dichloroethane, 1,1,1-trichloroethane, carbon tetrachloride, bromodichloromethane, trichloroethylene, benzene, tetrachloroethylene, and chlorobenzene. Devices examined included passive dosimeters manufactured by 3M, DuPont, and Abcor.

It is concluded that currently available passive monitors may be useful for monitoring ambient level volatile organics, but improvements in quality control by the manufacturers will be needed to insure consistently low device blanks before further evaluation can be made with the chlorinated hydrocarbons. The analytical methodology currently recommended for use with these devices is adequate for many compounds, but may be marginal for some, and further consideration of analysis alternatives is suggested. Assuming that reliably low blank levels can be achieved, detailed evaluation of device performance in the laboratory and under a variety of field conditions will be required before these devices can be recommended for routine ambient level monitoring.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
RELEASE UNLIMITED	UNCLASSIFIED	38
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (9-73)

DISCLAIMER

This report has been reviewed by the Environmental Monitoring Division, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD: BEGIN SECTIONS HERE

FORWARD

Measurement and monitoring research efforts are designed to anticipate potential environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has responsibility for: assessment of environmental monitoring technology and systems; implementation of agency-wide quality assurance programs for air pollution measurement systems; and supplying technical support to other groups in the Agency including the Office of Air, Noise, and Radiation, the Office of Toxic Substances, and the Office of Enforcement.

The determination of human exposure to toxic organic compounds is an area of increasing importance to EPA. The passive personal monitors evaluated in this study are possible candidate devices to be employed in future exposure monitoring studies. These devices are presently being employed in industrial hygiene and have many characteristics which make them potentially very useful in ambient air investigations. However, since the requirements for ambient air monitoring are more stringent than those for industrial hygiene, the present investigation was undertaken to identify possible problems with the commercially available devices when they are used in ambient air studies. Once identified, potential weaknesses may be corrected, resulting in valid use of the passive monitors in ambient exposure monitoring.

Thomas R. Hauser, Ph.D
Director
Environmental Monitoring Systems Laboratory
Research Triangle Park, North Carolina 27711

BOTTOM OF IMAGE AREA, OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
BEGIN LAST LINE OF TEXT
3/8"

EPA-287 (Cin.)
(4-76)

BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD BEGIN SECTIONS HERE

ABSTRACT

A laboratory investigation was conducted to determine the potential utility and limitations for the use of commercially available passive dosimeters for monitoring volatile organic compounds at ambient levels. Test compounds included chloroform, 1,2-dichloroethane, 1,1,1-trichloroethane, carbon tetrachloride, bromodichloromethane, trichloroethylene, benzene, tetrachloroethylene, and chlorobenzene. Devices examined included passive dosimeters manufactured by 3M, DuPont, and Abcor.

The use of passive dosimeters for multiple compound collection at ambient levels requires sensitivity and accuracy from the combined collection and analytical system at concentrations several orders of magnitude lower than the originally intended use of these devices. With normal background levels of chlorinated hydrocarbons for example, the expected 24-hour samples would be of the order of a few tens of nanograms of mass collected. This implies the need for device and solvent blanks of no more than a few nanograms per compound, and analytical sensitivity as low as picograms, depending on the desorption method.

In the current work, solvent desorption using 5 percent carbon disulfide in methanol was used, and the required detection sensitivity was attained using a series combination of electron capture and photoionization detectors. The complimentary selectivities of this detector pair yielded additional benefits in identification of chromatographic peaks. Desorption efficiencies were relatively constant over the range of concentrations of interest, but varied from about 85 percent for carbon tetrachloride to about 15 percent for chlorobenzene.

Blank levels for trichloroethylene, 1,1,1-trichloroethane, tetrachloroethylene, and carbon tetrachloride were generally high for all three devices, ranging from tens of nanograms for the DuPont badge to micrograms for some compounds on the Abcor badge. Other compounds were found with particular badges, and the blank levels were generally quite variable.

Tests of packaging integrity generally indicated good protection of the devices from contamination prior to use, but one case of a poor seal was found with a 3M badge.

Results showed clearly that the polymeric badge holders can serve as both sinks and sources for many of the volatile organic compounds. Badge holders must therefore be subject to the same quality control procedures as the sorbent strips, and the holders should not be reused.

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

It is concluded that currently available passive monitors may be useful for monitoring ambient level volatile organics, but improvements in quality control by the manufacturers will be needed to insure consistently low device blanks before further evaluation can be made with the chlorinated hydrocarbons. The analytical methodology currently recommended for use with these devices is adequate for many compounds, but may be marginal for some, and further consideration of analysis alternatives is suggested. Assuming that reliably low blank levels can be achieved, detailed evaluation of device performance in the laboratory and under a variety of field conditions will be required before these devices can be recommended for routine ambient level monitoring.

TYPING GUIDE SHEET
BEGIN FIRST LINE OF TEXT HERE
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD: BEGIN SECTIONS HERE
9-1/8"

CONTENTS

Forward iii
Abstract iv
Figures vii
Tables vii

1. Introduction 1
2. Conclusions and Recommendations 2
3. Definition of Technical Problem 4
   General Considerations 4
   Analytical Requirements 5
   Chemical Applicability 5
4. Experimental Methods 7
   Analysis Procedures 7
   Gas Chromatograph 7
   Detectors 7
   Desorption 10
   Standards 10
   Devices 11
5. Results 12
   General Observations 12
   Detection Limits 12
   Badge Blanks 14
   Desorption Efficiencies 14
   Packaging Integrity 18
6. Applicability of Tested Devices to Ambient Air Monitoring . 26

References 30

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

FIGURES

Number		Page
1	Approximate Gas Chromatographic Detector Ranges. . . .	8
2	Sample Chromatogram for Subject Compounds.	9

TABLES

1	Relative GC Detector Sensitivities and Detection Limits for Subject Compounds.	13
2	DuPont Badge Blanks.	15
3	3M Badge Blanks.	16
4	ABCOR Badge Blanks	17
5	Desorption Efficiencies of DuPont Collectors	19
6	Contamination of Collectors by Exposed DuPont Badge Holders.	20
7	Contamination of Collectors by Exposed 3M Badge Holders	21
8	Contamination of Collectors by Exposed ABCOR Badge Holders.	22
9	DuPont Packaging Materials Permeability Test	24
10	3M Packaging Materials Permeability Test	25
11	Lower Useful Exposure Levels for DuPont Badge.	28
12	Comparison of Lower Useful Limits of DuPont Badge with Ambient Conditions.	29

BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD; BEGIN SECTIONS HERE

SECTION 1

INTRODUCTION

Over the past decade, pollutant sampling methodology has undergone a natural development from generalized stationary source monitoring techniques to specialized mobile and stationary monitoring of large areas or regions to portable localized monitoring equipment. While all phases of pollution monitoring remain important, there has recently been increased emphasis on the need for direct determination of pollutant exposures for individuals in different kinds of environments. In this regard, portable battery-driven pumping (active) systems have been demonstrated for use in monitoring toxic organic compounds in industrial environments; and, more recently, several more convenient passive (no pump) devices have been evaluated for specialized applications in the workplace (1-7). A review (1) of characteristics of these devices has recently been prepared by Battelle Columbus Laboratory for the Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Research Triangle Park.

These passive devices depend upon well-characterized diffusion- or permeation-limited sampling of the air rather than pump sampling. The pollutants are collected on a suitable sorbent such as activated charcoal. Because of their small size (generally less than 30 cc in volume), low weight, low cost and the absence of pumps, batteries, tubing, etc., they are ideally suited for consideration as personal monitors. In practice, it is envisioned that these passive monitors could be used conveniently by an individual to determine true, time-weighted average pollutant exposures.

Although these devices have been tested to a limited extent with respect to monitoring of relatively high organic pollutant concentrations in workplace environments (ppm levels), no evaluation has been made of their applicability for sampling ambient concentrations (ppt to ppb levels) of volatile organic pollutants. The purpose of this program was to apply certain critical laboratory tests to the commercially available devices to determine their applicability to ambient air monitoring requirements. The critical laboratory tests included collector contamination determinations, desorption studies, and determination of storage effects. These test results indicated problems that will be encountered in later, more extensive laboratory and/or field studies. This study was restricted to nine organic compounds: chloroform, carbon tetrachloride, 1,2-dichloroethane, 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, bromodichloromethane, benzene, and chlorobenzene. These compounds represent a variety of volatile organic classes as well as toxicities of interest to EPA.

OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

TYPING GUIDE SHEET
BEGIN FIRST LINE OF TEXT HERE
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD. BEGIN SECTIONS HERE

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

A study has been made of the potential problem areas associated with the use of commercially available passive devices for ambient monitoring of volatile organic substances. This study has encompassed analytical problems as well as limitations associated with the construction of the devices. The following conclusions have been reached as a result of this study:

(1) The currently common use of the flame ionization detector (FID) detection for gas chromatographic analysis of organics is not sensitive enough for use with 24 hour ambient samples collected by passive devices. However, with the exception of a few special cases, most organics can be analyzed using the combination of electron capture detector (ECD) and photoionization detector (PID) employed in this study. However, improvement in the general analytical methodology is recommended.

(2) The use of carbon disulfide as the desorbing solvent for charcoal collectors in passive monitors is not recommended with electron capture detection, but a mixed solvent consisting of 5 percent CS_2 in methanol is useful for many compounds. Depending on the nature of the compounds being analyzed, other solvents may be necessary in order to achieve good desorption efficiencies. For example, desorption efficiencies with this solvent are less than 60 percent for tetrachloroethylene, benzene and chlorobenzene. In any case, it is imperative that solvent purity be checked carefully.

(3) All three commercially available badges (DuPont, 3M, Abcor) have blank levels of some chlorinated hydrocarbons that are too high and too variable to permit their use in ambient level sampling of these compounds. However the same badges show potential for monitoring certain other specific compounds, such as benzene, for which the blank levels are low and anticipated ambient levels are relatively high. One manufacturer has suggested that the badges become contaminated during the packaging procedure. It should be possible to eliminate this problem, but this conjecture needs to be evaluated. In any case, quality control procedures used by the manufacturers will need to be up-graded if these devices are to be used under ambient conditions.

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

EPA-287 (Cln.)
(4-76)

(4) The plastic holders that are used in these devices are natural sinks and/or sources for volatile organics. However, the significance of this potential source of error cannot be fully evaluated until "clean" carbon strips can be made available by the manufacturers. It is possible that metal holders may eliminate this potential problem, and one manufacturer has indicated that such a holder is commercially feasible.

(5) The lack of protective packaging of the Abcor badge holder and the tendency for the carbon strip to swell and disintegrate in some solvents makes quantitative analysis with this badge at ambient levels doubtful.

(6) Although the 3M system is difficult to adapt to conventional automated GC sampling, and its diffusion barrier is not rugged, this badge might be useful for ambient level sampling providing that blank levels can be suitably reduced.

(7) The DuPont badge is the most rugged system tested, and it could be adapted to ambient level sampling providing low blank levels can be achieved.

The DuPont and 3M badges appear to hold the most promise for use in ambient level sampling, and it is recommended that these devices be given further consideration. First, low and consistent blank levels must be demonstrated. Second, the badge holders must not interfere with accurate sampling by either desorption of contaminants to the carbon strips or by appreciable sorption of pollutants being sampled. Assuming that these requirements can be successfully completed, it is recommended that these devices be thoroughly evaluated for their sampling accuracy and precision in extensive laboratory tests that are conducted over a range of exposures illustrating typical ambient concentrations of both organic and inorganic pollutants. Assuming that one or both of these badges can be rated as satisfactory in these laboratory tests, they should then be tested under field conditions using the best available independent methods for reference.

It is recommended that further studies of desorption effeciencies with a variety of solvents and thermal desorption be initiated. Methods of producing "clean" collectors must be developed, either by thermal methods or polar solvent extraction, e.g., liquid carbon dioxide. Investigation of analytical methods to determine the collected organics without extraction should also be investigated.

BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD, BEGIN SECTIONS HERE

SECTION 3

DEFINITION OF TECHNICAL PROBLEM

General Considerations

While there are strong indications that passive monitors can be used for monitoring particular organic compounds in workplace environments (1-5), the technical problem of monitoring multiple organic compounds at ambient concentrations is quite different. The fact that ambient concentrations (ppt to ppb) are generally several orders of magnitude lower than those for which the devices were originally intended (ppm) is fundamental to most of the technical problems that need to be considered. The total system involves both device performance and analytical methodology, with elements of each being highly interactive. Specific areas of concern for ambient monitoring are:

9-1/8"

1. Analytical Methodology
   a. Selectivity
   b. Sensitivity
   c. Precision and Accuracy
   d. Desorption Efficiency
2. Device Parameters
   a. Sorption Efficiency
   b. Blank Levels
   c. Reproducibility
   d. Interferences
   e. Time Stability of Sorbed Species

Some of these factors such as the reproducibility and accuracy of device performance can only be fully evaluated in more detailed laboratory and field tests. However, determination of device blanks, desorption efficiencies, and effects of storage can be employed for screening of devices and determination of developmental needs. The extent and variability of the blank levels of the device sorbents is particularly crucial to their application in collecting very low absolute amounts of organic pollutants. High and variable blank levels can effectively "swamp out" ambient level pollutants. Equally important are the desorption efficiencies which if low and highly variable make the analytical results highly inaccurate.

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA, OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD: BEGIN SECTIONS HERE

Analytical Requirements

The requirements that must be met can be defined to some extent by the expected loading of pollutants to be collected in a 24-hour sample. The collection rate (effective pumping rate) for the common passive devices is of the order of 50 cc/min, with some small variations possible depending on the compound in question and the particular device that is used. Typical ambient air concentrations of volatile pollutants such as the chlorinated hydrocarbons and benzene are of the order of tens to hundreds of parts per trillion. Using a value of 100 ppt and a nominal molecular weight of 100, the expected 24-hour collection of such a compound would be about 30 ng.

The usual approach for analysis of these devices is to use solvent (usually carbon disulfide) extraction, with only about 0.1 percent (1 μℓ) of the solution being used for chromatographic analysis. Thus, the analytical method must be sensitive at least to 3 pg and preferably to 0.3 pg in order to detect variations in the normal levels. This loading also suggests limits on the blank levels that are desirable for the devices. In general, average blanks should be no more than 10 percent of the expected loading, or no more than 3 ng per device. Variation in the average blanks should not exceed ± 1 to 2 ng per device. Any solvents used also should contain no more than 3 ng/desorption volume. Inasmuch, as any errors associated with measurement of the apparent loading, the device blank, the solvent blank, and the desorption efficiency are cumulative with respect to the error in the true device loading; these allowances of 3 ng each for the blanks are quite liberal, but they provide a preliminary basis for judging minimal acceptance.

Any nominal requirement set for the desorption efficiency is obviously interactive with the sensitivity required for the analytical method; the lower the desorption efficiency, the greater the sensitivity that is required for a given loading. If the desorption efficiencies are not highly variable, then the analytical data may be corrected for values less than 100 percent. However, the desorption efficiencies are not precisely determined due to error propagation from both the spiked and control sorbent.

Chemical Applicability

With use of passive devices in the workplace, it is often adequate if only one or two compounds are considered in the overall sampling and analysis scheme. However, ambient sampling is more likely to be concerned with a wide range of compounds. Thus, the device and the analytical procedure should serve equally well for compounds of differing volatility, polarity, chemical functionality, and molecular size. It is unlikely that a perfectly general approach can be identified, but it is desirable that the sampling and analysis scheme not be overly limited by requiring separate calibration for each particular combination of chemical exposures. With diffusion limited devices of a given geometry, the sampling rate is a function solely of the diffusion coefficient of the compound in air. With permeation, both the diffusion coefficient and the solubility of the compound in the permeation membrane affect the sampling rate. Thus, passive devices based on the

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

EPA-287 (Cin.)
(4-76)

BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD; BEGIN SECTIONS HERE
6-1/2"
9-1/8"
BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"
PAGE NUMBER
EPA-287 (Cin.) (4-76)

use of a permeation barrier are expected to be more susceptible to variations in physicochemical nature of the pollutant than are devices that depend solely on diffusion.

Gas chromatography with sensitive electron capture and photoionization detectors is the most inexpensive and general method for quantitation of volatile organics. Qualitative compound verification by GC-MS or other methods is necessary, however. In the current work, the following compounds were selected as target compounds: chloroform, 1,2-dichloroethane, 1,1,1-trichloroethane, carbon tetrachloride, bromodichloromethane, trichloroethylene, tetrachloroethane, benzene, and chlorobenzene. This set was not meant to be all inclusive for ambient organics but was selected to give a range of molecular classes and toxicity.

BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD; BEGIN SECTIONS HERE

SECTION 4

EXPERIMENTAL METHODS

ANALYSIS PROCEDURES

Gas Chromatograph

Analyses for this program were carried out using a Varian Model 3700 gas chromatograph, coupled to two Hewlett-Packard Model 3380 integrators for data readout. Nitrogen, at a flow rate of 30 cc/min was used as the carrier gas. A number of column packings are available commercially for the separation of the chlorinated hydrocarbons. These include methyl and phenyl silicones, graphitized carbons, Bentone, and various combinations of these materials. Based on preliminary trials with several of these combinations, a 2.44 m Carbopack-B column with 1 percent SP-1000 was selected. Satisfactory results were obtained with this column using a temperature program consisting of a 10 minute hold at 100°C followed by a ramp of 4°C/min to 180°C.

Detectors. The most commonly used gas chromatographic detector for organic compounds is the flame ionization detector (FID). However, this detector does not have sufficient sensitivity for use with picogram (pg) samples. Many of the subject compounds can be detected with very good sensitivity using an electron capture (ECD) detector, but the sensitivity of this detector is quite variable depending on chemical structure. Compounds such as vinyl chloride, benzene, and chlorobenzene are not detected by the ECD. The newly developed photoionization detector (PID) is more sensitive than FID for hydrocarbons, it can detect benzene and chlorobenzene, and some degree of selectivity can be gained through choice of source energy. A comparison of the ranges of applicability for these detectors if given in Figure 1.

Inasmuch as both the ECD and PID are non-destructive detectors, the two were connected in series in this program to obtain essentially simultaneous readout of both ECD and PID responses from a given sample. By using a 10.2 eV source for the PID, which is relatively insensitive to the highly chlorinated compounds; relatively selective responses from the two detectors were obtained. This has proven useful in identifying regions of the chromatograms where a less selective detector such as the FID would sense interferring peaks since differentiation can be achieved by both the column and the detector pair. Figure 2 shows dual chromatograms (ECD and PID) obtained for the subject list of compounds.

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

EPA-287 (Cin.)
(4-76)

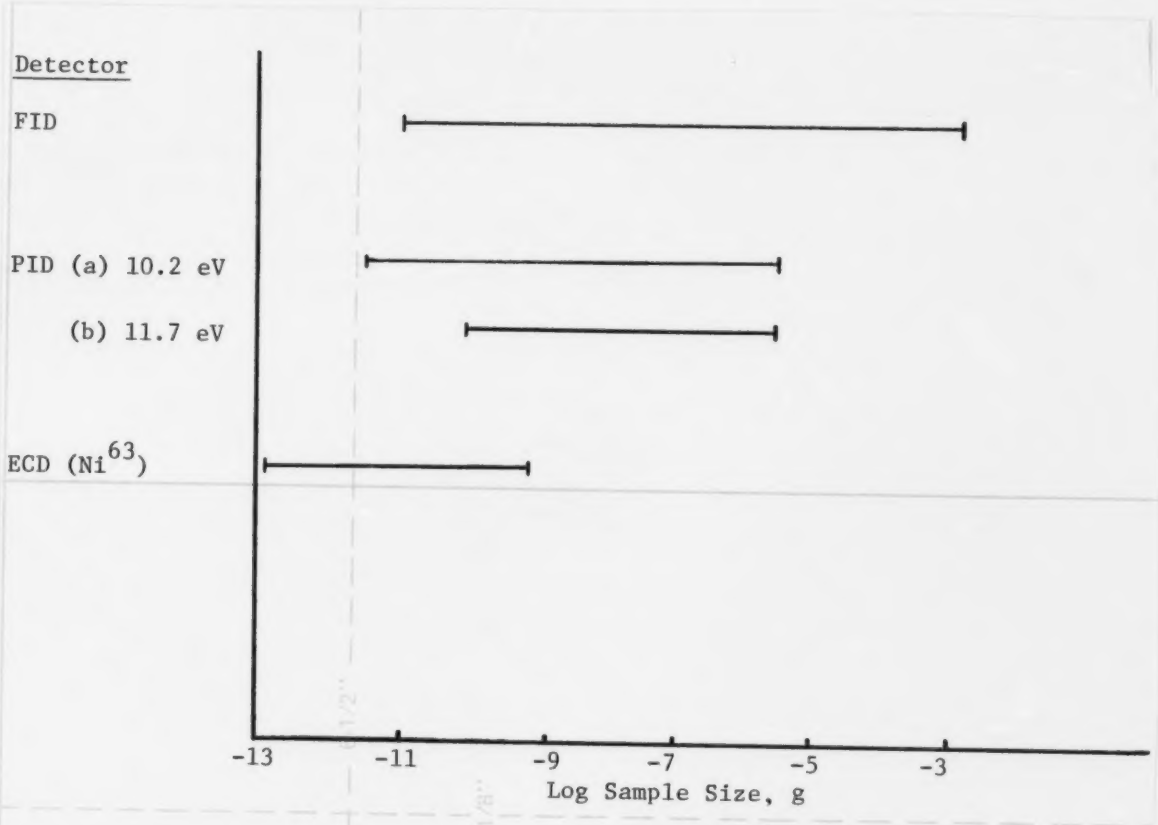
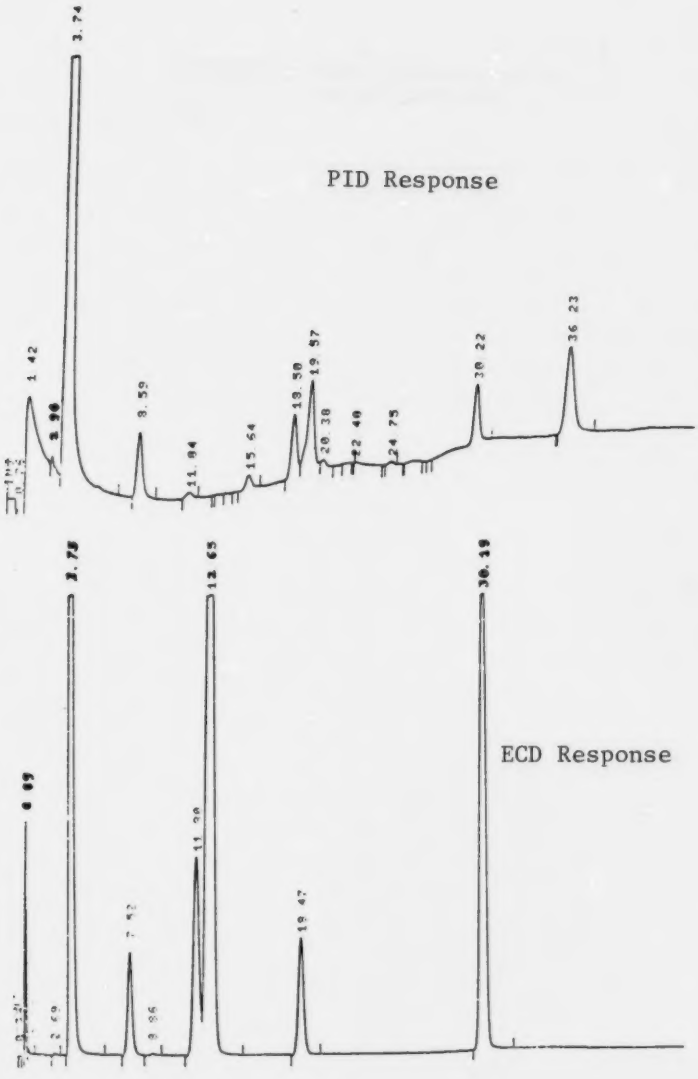


FIGURE 1. APPROXIMATE GAS CHROMATOGRAPHIC DETECTOR RANGES



Elution Sequence:

Compound	Retention Time, min ECD	PID
Chloroform	7.52	N.D.
1,2-Dichloroethane	8.86	N.D.
1,1,1-Trichloroethane	11.80	11,84
Carbon tetrachloride	12.65	N.D.
Bromodichloromethane	(14.73)(Not Shown)	N.D.
Trichloroethylene	18.47	18.50
Benzene	N.D.	19.57
Tetrachloroethylene	30.19	30.22
Chlorobenzene	N.D.	36.23

FIGURE 2. SAMPLE CHROMATOGRAM FOR SUBJECT COMPOUNDS

BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD; BEGIN SECTIONS HERE

Desorption

There are essentially two choices for methods of desorption of adsorbed species from activated charcoal: (1) thermal desorption and (2) solvent desorption. Because of the wide range of variability possible with organic compounds with respect to volatility, polarity, chemical functionality, etc., it is unlikely that any one technique or any one solvent will be equally effective for desorption of all possible compounds. Both methods have their advantages and deficiencies, and it is likely that the use of one or the other may depend on the particular class of compounds being sought. In any case, the desorption efficiency must be determined, preferably using sample sizes, concentrations, and contaminations that simulate real samples.

Carbon disulfide is commonly recommended for desorption of passive devices that have been used for industrial level sampling, and the use of this solvent thus provides a continuum with prior experience. However, this solvent cannot be used in pure form with electron capture detection because of the excessive response of the detector and appreciable solvent tailing on most columns. Also, even the best grade of carbon disulfide that we have examined (Baker Instra-Analyzed Reagent) contains appreciable impurities that are evident by ECD and PID detection. We have therefore, sought to retain the excellent desorbing properties of carbon disulfide while minimizing its drawbacks by employing mixtures of carbon disulfide in methanol. The latter solvent yields minimal response with both ECD and PID, and there are several commercially available grades that are "clean" enough for chromatographic analysis. Most of the current work was performed using a mixture of 5 percent carbon disulfide in Baker Resi-Analyzed methanol. With this mix, typical solvent blanks for methylchloroform, carbon tetrachloride and tetrachlorethylene are 2, 0.5, and 10 pg/μl respectively. Other contaminants are noted, but these do not correspond to the remaining compounds on the target list. This solvent yields good desorption efficiencies for most of the compounds (see section on Desorption Efficiencies for data), but efficiencies for benzene and chlorobenzene may be too low. Thus, examination of other solvents, or possibly other desorption techniques may be required for these compounds.

Standards

Standards for this program were prepared by successive dilutions of stock solutions. Stock solutions were prepared using either gravimetric or volumetric addition of the solute to a small portion of the solvent, followed by dilution to volume. Gravimetric additions are probably more accurate, but the volumetrically referenced standards were generally more convenient and compared to the gravimetric standards to within a few percent. The more volatile components of the target set of compounds can easily evaporate from the standard solutions. Consequently, standards need to be prepared freshly, at least on a weekly basis.

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

DEVICES

There are currently four passive devices that are commercially available and which might be considered useful for general organic vapor monitoring. These are manufactured by 3M, DuPont, Abcor, and Real. The Real badge is a permeation device that has been tested extensively for vinyl chloride, but which requires special calibration of each badge individually for use with other organics. Because of this and the relatively high cost of the badge, it was not considered further.

BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD, BEGIN SECTIONS HERE

SECTION 5

RESULTS

GENERAL OBSERVATIONS

While the three types of passive devices evaluated are similar in function, there are distinctive features of each that could be undesirable. The Abcor badge was found to be quite adsorbent with respect to several solvents, and required excess solvent addition in order to maintain an appreciable free volume of solvent in the analytical work-up. Also, it was noted that the Abcor badge tended to disintegrate in some solvents. The 3M system is designed for addition of the desorbing solvent directly to the badge holder, and a volume of 1.5 ml of solvent is recommended by the manufacturer. Such a system is awkward with respect to utilization of automatic GC injection, and presents the possibility of extraction of compounds from the badge holder itself. The 3M system also utilizes a membrane diffusion barrier that could be subject to damage during use. The DuPont design is the most rugged and is probably best suited for routine analysis because of the size and shape of the charcoal strip. However, the DuPont strip does have to be rolled, folded, or otherwise manipulated by hand for insertion into a GC analysis vial. This presents the possibility of contamination during analytical workup. For this study a simple tool was devised to facilitate this manipulation. However, the manufacturer does not supply such a tool.

DETECTION LIMITS

Relative sensitivities of the two detector systems and detection limits under the particular run conditions are shown in Table 1. In this case, the detection limit is defined as the concentration that corresponds to a signal two standard deviations above the apparent zero level. For those compounds detected by the ECD, their detection limits are in the range of 0.4 to 5 ng/badge except in the case of 1,2-dichloroethane. For those compounds to be detected by the PID, the detection limits are marginal, but probably useful. Obviously some further development in methodology would be desirable to enhance these detection limits. These detection limits refer to injection of only 1 µl of sample, a procedure adopted for consistency with current methodology for other applications of the passive devices. Samples of up to 10 µl could be used in some cases. Another approach that would be useful for enhancing both selectivity and detection limits would be the use of capillary column chromatography. Also shown in Table 1 are approximate detection limits for many of the same compounds as determined by FID in this laboratory. In all cases, the ECD/PID pair is more sensitive than the FID.

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION
FO
AND
TRATIONS
3/8"

EPA-287 (Cin.)
(4-76)

TABLE 1. RELATIVE GC DETECTOR SENSITIVITES AND DETECTION LIMITS FOR SUBJECT COMPOUNDS[a] (at ng → pg levels)

	Detector Sensitivities					
	Electron Capture		Photoionization (10.2 eV)		Flame Ionization	
	RS[b]	DL[c]	RS[b]	DL[c]	RS[b]	DL[c]
Chloroform	1.0	5.0	0.0	--	0.1	1000
1,2-Dichloroethane	0.030	170	0.0	--	0.29	345
1,1,1-Trichloroethane	3.1	1.6	0.05	200	0.19	525
Carbon Tetrachloride	14	0.36	0.0	--	0.09	1100
Bromodichloromethane	6.4	0.78	0.0	--	--	--
Trichloroethylene	1.4	3.6	0.34	29	0.21	475
Benzene	0.0	--	1.0	10	1.0	100
Tetrachloroethylene	7.0	0.71	0.30	33	0.17	510
Chlorobenzene	0.0	--	0.55	18	--	--

(a) Mass basis; measured under conditions for detection of complete list of chemicals (not optimized for particular compound).

(b) Sensitivity relative to chloroform (ECD) or benzene (PID and FID).

(c) Approximate detection limits in ng/badge using 0.1 percent of sample for analysis. GC injection volume was 1 μℓ.

BEGIN FIRST LINE OF TEXT
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA
6 1/2"

BADGE BLANKS

Contamination of the charcoal collectors was determined for each of the three types of badges. Badges for this purpose were selected at random from supplies purchased from the manufacturers and were run in triplicate. Additional blanks also were run periodically during the course of the program as a part of the general procedures in performing other experiments. Results of these experiments are shown in Tables 2 to 4 in units of ng/badge. Although these data are uncorrected for desorption efficiencies, it is obvious that none of the badges has sufficiently low blank levels to be useful for monitoring of all of the compounds. The DuPont badges apparently are clean enough to determine ambient levels of chloroform, carbon tetrachloride, trichloroethylene, and bromodichloromethane. However, the blank levels are so variable in all badges that use of an average or median value in correcting apparent collection values is of limited value. It is noteworthy that all three badges show evidence of chlorinated hydrocarbons, which are common solvents, but little benzene or chlorinated benzenes. This suggests a specific primary source for these blanks rather than a generalized contamination. It is quite possible that the source of this contamination can be identified and eliminated.

DESORPTION EFFICIENCIES

Attempts were made to determine the desorption efficiencies of the subject compounds by two different methods. In the first method, a 1.9 liter stainless steel cannister was coupled to the GC via a gas sampling valve having graphite seats. This canister could be flushed with nitrogen and then loaded with a given compound or mixture of compounds to the desired concentration level. A stainless steel vial containing a test charcoal strip was then attached to the cannister, and was allowed to adsorb the test compound for periods of time ranging from a few hours to a day. The change in concentration within the canister was taken as being indicative of the amount adsorbed by the charcoal strip. Comparison of this value with the results of analysis of the strip yielded apparent desorption efficiencies.

BEGIN LAST LINE HERE
BOTTOM OF IMAGE AREA, OUTSIDE MENSION
DROPPED HEAD, BEGIN SECTIONS HERE

Initial results obtained with the use of chloroform as the test compound and 5 percent carbon disulfide in Baker Resi-Analyzed methanol as the desorbing agent yielded consistent desorption efficiencies (DEs) of 70 $\pm$ 2 percent on DuPont collector for chloroform at loadings of about 100 to several thousand ng/badge. However, attempts to apply this method at lower loadings to be expected in ambient sampling or with mixtures of the subject compounds were confounded by unstable readings of the concentrations of the test compounds in the canister.

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA, OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

EPA-287 (Cin.)
(4-76)

TABLE 2. DUPONT BADGE BLANKS[a]
(ng/badge)

Compound	Badge No. 1	2	3	4	5	6	7	Median and Range[b]
Chloroform	< 5.0	<5.0	30	< 5.0	108	< 5.0	41	<5.0(< 5.0 to 108)
1,2-Dichloroethane	<170	<170	<170	<170	<170	<170	<170	<170
1,1,1-Trichloroethane	22	1.6	19	23±2	10	39±0.5	68	22(<1.6 to 68)
Carbon Tetrachloride	<0.36	14±1	6.0	13±0.4	3.0	13±0.4	<0.36	6.0(<0.36 to 14)
Bromodichloromethane	<0.78	<0.78	<0.78	<0.78	<0.78	<0.78	<0.78	<0.78
Trichloroethylene	45	25 ±1	<3.6	<3.6	19	<3.6	4.0	4.0(<3.6 to 45)
Tetrachloroethylene	<0.71	41±1	(c)	15±3	(c)	24±0.5	40	24(<0.7 to 41)
Benzene	<10	<10	<10	<10	<10	<10	<10	<10
Chlorobenzene	<18	<18	<18	<18	<18	<18	<18	<18

(a) Uncorrected for desorption efficiencies.
(b) Range in Parenthesis.
(c) Improper integration, data not useful.

TABLE 3. 3M BADGE BLANKS[a]
(ng/badge)

Compound	Badge No. 1	2	3	4	Median and Range[b]
Chloroform	<5.0	13.5	16.1	16.2	15(<5.0 to 16.2)
1,2-Dichloroethane	<170	<170	<170	<170	<170
1,1,1-Trichloroethane	233	178±2	292±23	246±7	240(178 to 292)
Carbon Tetrachloride	5.0	4.8±0.02	7.4±0.5	5.5±0.4	5.3(4.8 to 7.4)
Bromodichloromethane	<0.78	<0.78	<0.78	<0.78	<0.78
Trichloroethylene	250	194±17	305±37	205±14	230(194 to 305)
Tetrachloroethylene	20	9.9	141±8	9.6	15(9.6 to 141)
Benzene	<10	<10	<10	<10	<10
Chlorobenzene	<18	<18	<18	<18	<18

(a) Uncorrected for desorption efficiencies.
(b) Range in parenthesis.

TABLE 4. ABCOR BADGE BLANKS [a]
(ng/badge)

Compound	Badge No			Median and Range [b]
	1	2	3	
Chloroform	<5.0	<5.0	<5.0	<5.0
1,2-Dichloroethane	<170	<170	<170	<170
1,1,1-Trichloroethane	443	400	680	443(400 to 680)
Carbon Tetrachloride	1720	220	230	230(220 to 1720)
Bromodichloromethane	<0.78	<0.78	<0.78	<0.78
Trichloroethylene	430	110	120	120(110 to 430)
Tetrachloroethylene	44	20	50	44(20 to 50)
Benzene	<10	<10	<10	<10
Chlorobenzene	<18	<18	<18	<18

(a) Uncorrected for desorption efficiencies.
(b) Range in parenthesis.

BEGIN FIRST LINE OF TEXT
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE

The second method that was used is the so-called phase equilibrium method (4). In this approach, a badge is placed in a sealed glass vial along with 1 ml of the desorbing agent containing a known loading of the test compounds. A similar vial containing 1 ml of the same solution is used as a reference. Solutions were prepared by dilution of a stock mixture, and badges were allowed to equilibrate overnight in contact with the solutions. Comparison of the badge solution with the reference solution then gives the desorption efficiencies at each concentration level. Results of this work with DuPont collectors at various nominal concentrations are shown in Table 5. Only 1,1,1-trichloroethane, carbon tetrachloride, chloroform, and trichloroethylene have DEs greater than 60 percent. However, all the results were variable. Obviously, some variation in desorption efficiencies is to be expected depending on the nature of the test compounds, and it may well be that one particular solvent will not be generally applicable. As for the variations of DEs as a function of concentration, it should be noted that each DE is the result of two separate analyses, each of which is subject to a probable error of about 5 percent. Variations in DEs of about 10 percent therefore are probably not significant with respect to any anticipated concentration dependence. Since the blank collectors were found to have highly variable levels, some of the apparent DE variability may be due to the blanks rather than to an intrinsic variability.

PACKAGING INTEGRITY

Both the DuPont and 3M collectors are supplied already mounted in their holders and packaged in sealed aluminum-organic laminate pouches. The Abcor badge is provided separately and is not protected from exposure during shipping or storage. In order for these badges to be useful for ambient level sampling, the packaging materials must be impermeable to compounds of interest, and the badge holders must not contribute contaminants to the carbon strips. Two experiments were therefore conducted to test packaging integrity and sorption/desorption of the badge holders. In the first of these experiments, three badge holders of each type were chosen at random from our bulk supplies and were placed in a closed metal container along with a small vial containing a mixture of all of the test compounds. This severe exposure was continued for about one month. The holders were then removed and were allowed to "outgas" in a laboratory atmosphere for a period of four days (non-working laboratory; extended weekend period). Unexposed carbon strips were then inserted in their respective holders, and each badge was placed in a sealed glass jar for 24 hours. The strips were then removed and analyzed with results (µg/badge) as shown in Tables 6 to 8. For most of the compounds, the apparent GC responses were well beyond the linear range of the detector; so that the data given in Tables 6 to 8 are only lower limits, and it is quite apparent that the badge holders can serve as both sinks and sources for the test compounds. This is not a surprising result, considering the chemical nature of the holders and the test compounds. It emphasizes the need for protection of the holders during shipping and storage and the need for quality assurance by the manufacturer with respect to the state of the holders at the time of packaging.

BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION
BEGIN LAST LINE OF TEXT
DROPPED HEAD; BEGIN SECTIONS HERE
FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.) (4-76)

TABLE 5. DESORPTION EFFICIENCIES OF DUPONT COLLECTORS
(PERCENT RECOVERY)

Compound	Spike Concentrations (µg/Badge) 120	25	5	2.5	1	0.2	0.05	Median and Range[c]
Chloroform	(1.02)[a]	77	71	85	74	(90)	79	79(71 to 102)
1,2-Dichloroethane	-[b]	78	51	(52)	-	-	-	52(51 to 78)
1,1,1-Trichloroethane	78	82	81	89	69	(110)	-	82(78 to 110)
Carbon Tetrachloride	94	84	81	87	55	69	68	81(55 to 94)
Trichloroethylene	65	55	50	60	51	63	71	60(50 to 71)
Benzene	45	32	45	57	58	(130)	48	48(32 to 130)
Tetrachloroethylene	52	32	34	31	30	30	32	32(30 to 52)
Chlorobenzene	29	14	17	15	-	-	-	16(14 to 29)

(a) Questionable data in parenthesis.
(b) No useable data.
(c) Range in parenthesis.

TYPING GUIDE SHEET
BEGIN FIRST LINE OF TEXT HERE
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD; BEGIN SECTIONS HERE
6-1/2"
BEGIN LAST LINE OF TEXT
3/8"
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
PAGE NUMBER
EPA-287 (Cin.)
(4-76)

TABLE 6. CONTAMINATION OF COLLECTORS BY EXPOSED DUPONT BADGE HOLDERS[a]
(μg/badge)

Compound	Badge No 1	2	3	Median
Chloroform	>11	>11	>11	>11
1,2-Dichloroethane	6	6	12	6
1,1,1-Trichloroethane	>8	>7.4	> 9.7	>8
Carbon Tetrachloride	> 5.2	>4.9	> 5.1	> 5.1
Bromodichloromethane	> 7.8	>7.0	> 7.8	> 7.8
Trichloroethylene	>28	>25	>29	>28
Tetrachloroethylene	>17	>14	>17	>17

(a) Uncorrected for desorption efficiencies.
(b) > indicates data beyond linear ECD range.

TYPING GUIDE SHEET
BEGIN FIRST LINE OF TEXT HERE
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD; BEGIN SECTIONS HERE
6 1/2"
BEGIN LAST LINE OF TEXT
3/8"
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
PAGE NUMBER
EPA-287 (Cin.) (4-76)

TABLE 7. CONTAMINATION OF COLLECTORS BY EXPOSED 3M BADGE HOLDERS[a]
(μg/badge)

Compound	Badge No. 1	2	3	Median
Chloroform	5.8	5.6	6.5	5.8
1,2-Dichloroethane	4.4	4.1	4.9	4.4
1,1,1-Trichloroethane	1.1	0.96	1.3	1.1
Carbon Tetrachloride	0.65	0.63	0.73	0.65
Bromodichloromethane	>4.9[b]	>4.8	>5.4	>4.9
Trichloroethylene	>9.9	>9.4	>11.0	>9.9
Tetrachloroethylene	>4.5	>4.5	>4.4	>4.5

(a) Uncorrected for desorption efficiencies on blanks.
(b) > indicates data beyond ECD linear range.

BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD; BEGIN SECTIONS HERE

TABLE 8. CONTAMINATION OF COLLECTORS BY EXPOSED ABCOR BADGE HOLDERS[a]
(ug/badge)

Compound	Badge No. 1	2	3	Median
Chloroform	1.7	1.8	2.1	1.8
1,2-Dichloroethane	2.2	2.5	3.3	2.5
1,1,1-Trichloroethane	3.0	3.4	3.7	3.4
Carbon Tetrachloride	0.40	0.27	0.21	0.27
Bromodichloromethane	2.0	2.2	2.6	2.2
Trichloroethylene	4.7	4.9	5.4	4.9
Tetrachloroethylene	>6.8	>6.7	>7.1	>6.8

(a) Uncorrected for desorption efficiencies on blanks.
(b) > indicates data beyond linear range of ECD.

6-1/2"
9-1/8"
BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

PAGE NUMBER
EPA-287 (Cin.)
(4-76)

In a second experiment related to materials integrity, three sealed pouches containing one previously unexposed collector each of the DuPont and 3M badges were subjected to a similar severe challenge. They were stored in contact with the vapors of the test compounds for about one month, and then the collectors were removed and analyzed. Results of these measurements are shown in Tables 9 and 10 (ng/badge). The results suggest some leakage by the pouches, but the data are not self-consistent. With the DuPont badges, we believe that the results may simply reflect the normal variability of the blanks rather than any consistent permeation of the packaging. With the first 3M badge, there is definite leakage of the pouch, indicating an imperfection in the pouch seal; but the carbon tetrachloride level is quite low. The other two 3M badges seem to reflect variations in the blank levels.

BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD; BEGIN SECTIONS HERE
6-1/2"
9-1/8"

TABLE 9. DUPONT PACKAGING MATERIALS PERMEABILITY TEST
(ng/badge)[a]

Compound	Badge No. 1	2	3	Median	Blank Comparison[b]
Chloroform	< 5	< 5	< 5	< 5	Y
1,2-Dichloroethane	<170	<170	<170	<170	Y
1,1,1-Trichloroethane	39	14	47	39	Y
Carbon Tetrachloride	29	19	32	29	N(2x)
Bromodichloromethane	3	2	10	3	N(3x)
Trichloroethylene	35	13	44	35	Y
Tetrachloroethylene	83	82	76	82	N(2x)

(a) Uncorrected for blanks
(b) Y = within range of blanks; N = out of blank range (relative factor)

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

EPA-287 (Cin.)
(4-76)

BEGIN FIRST LINE OF TEXT HERE
TYPING GUIDE SHEET
CENTER OF PAGE
TOP OF IMAGE AREA
DROPPED HEAD; BEGIN SECTIONS HERE
6-1/2"
9-1/8"

TABLE 10. 3M PACKAGING MATERIALS PERMEABILITY TEST
(ng/badge)[a]

Compound	Badge No. 1	2	3	Median	Blank Comparison
Chloroform	>11,000	<5	47	47	N(3x)
1,2-Dichloroethane	12,000	<170	<170	<170	Y
1,1,1-Trichloroethane	360	250	250	250	Y
Carbon Tetrachloride	10	6	6	6	Y
Bromodichloromethane	> 2,500	6	11	11	N(10x)
Trichloroethylene	6,300	250	270	270	Y
Tetrachloroethylene	59	48	28	48	Y

(a) Not corrected for blanks
(b) Y = within range of blanks; N = out of range (relative factor)
(c) Numbers with ">" sign indicate a chromatogram area beyond the linear range of ECD.

BEGIN LAST LINE OF TEXT
BOTTOM OF IMAGE AREA; OUTSIDE DIMENSION FOR TABLES AND ILLUSTRATIONS
3/8"

EPA-267 (Cin.)
(4-76)

SECTION 6

APPLICABILITY OF TESTED DEVICES TO AMBIENT AIR MONITORING

The significance of the analytical detection limits and blank levels in determining the potential utility of these badges for ambient air sampling must be considered relative to the limitations of air sampling that are achieved and the expected ambient levels of the particular compounds. Each of the devices considered is diffusion-limited in its sampling rate, and the mass (m in grams) of each substance collected over a given time period is given by

$$m = D\ (A/L) \cdot C \cdot t \qquad (1)$$

where D (cm^2/min) is the diffusion coefficient for the substance in air, A/L (cm) is the ratio of the total sampling area to the length of the diffusion channels, C is the concentration (g/cm^3) of species sampled in the air, and t is the sampling time in minutes. The values of A/L for the different badges differ according to the physical design of the system, but sampling rates on the order of tens of cm^3/min are normally achieved. Tabulations of sampling rates (DA/L) for individual compounds are normally available from the manufacturers. The concentration of a given species sampled in ppb-v is obtained by rearranging equation 1 and calculating the volume corresponding to the mass via the ideal gas law:

$$C\ (\text{ppb-v}) = \frac{10^9\ mRT}{Mt\ (DA/L)\ P} \qquad (2)$$

where M is the molecular weight of the compound, R ($cm^3 \cdot atm \cdot deg^{-1} \cdot mole^{-1}$) is the gas constant, P (atm) is the atmospheric pressure, and T is the temperature (K).

Because of the variability of the blanks and the fact that analyses performed near the detection limits are inaccurate; the lower useful limit for the devices was defined as ten times the median blank level or ten times the detection limit, whichever was greater. Correcting the actually measured values for desorption efficiencies, and selecting a sampling time of 24 hours at one atmosphere pressure and a temperature of 298°K, equation 2 becomes

$$C_{LL}\ (\text{ppb-v}) = \frac{17 \cdot 10^9\ m_{B\text{-}DL}}{DE \cdot (DA/L) \cdot M} \qquad (3)$$

where C_{LL} is the lower limit of concentration for which the badge is useful due to blank and/or detection limitations. The limiting mass ($m_{B\text{-}DL}$) is given in Table 9 or 10. As an example of application of equation 3, sampling rates and C_{LL} values calculated by equation 3 for the DuPont device are shown in

Table 11. With some variation, qualitatively similar results are obtained with reference to the other two types of badges. Both blank problems and detection limitations are responsible for the 0.1 to 7.0 ppb-v lower useful limits for the tested compounds.

The important criterion for determining the potential utility of the tested devices in ambient air applications is the ratio of the expected ambient concentrations to the lower useful concentration limits listed in Table 11. Singh et al. (9) recently reported ambient air levels of some 33 organic compounds found in three western cities (Oakland, Phoenix, Los Angeles) including the compounds investigated in this study. The mean values for Los Angeles, which are usually higher than the other cities, are listed in Table 12 along with the ratios of these ambient concentrations (C_A) to the C_{LL} values from Table 11. C_A/C_{LL} values of one or less indicate no potential ambient utility unless the ambient levels for a potential location are much higher than those in Table 12. Inasmuch as the standard deviations of the cited mean ambient levels are generally of the order of 50-75 percent, even ratios of one and one-half to two can be considered of marginal usefulness. Ratios greater than two indicate good potential. For the ambient concentrations cited, chloroform, chlorobenzene, tetrachloroethylene and 1,2-dichloroethane will not be detected in a 24 hour sampling period. Carbon tetrachloride and 1,1,1-trichloroethane fall into the somewhat marginal classification. However, benzene and trichloroethylene could be monitored in a 24 hour period with the present DuPont badge.

Obviously there are a number of possible improvements that could be made. Lower and more consistent blanks, i.e., better quality control by the manufacturers, would permit analysis at lower levels. Also some improvements in the analytical methodology (capillary chromatography, larger aliquots) are possible which could improve the detection limits by at least a factor of two. These two improvements alone would yield an excellent potential rating for all compounds tested except 1,2-dichloroethane and chlorobenzene on the DuPont badge.

TABLE 11. LOWER USEFUL EXPOSURE LEVELS FOR DUPONT BADGE [a]

Compound	Sampling Rate,[b] cm^3/min	C_{LL},[c] ppbv	Limiting Factor
Chloroform	79	0.11	Detection
1,2-Dichloroethane	81	7.0	Detection
1,1,1-Trichloroethane	60	0.58	Blank
Carbon Tetrachloride	74	0.11	Blank
Trichloroethylene	65	0.13	Blank/Detection
Benzene	71	0.65	Detection
Tetrachloroethylene	51	1.5	Blank
Chlorobenzene	66	2.5	Detection

(a) 24-hour sampling period.
(b) As cited by DuPont brochure, May 1981. Rate is with both covers removed.
(c) As defined by Equation 3.

TABLE 12. COMPARISON OF LOWER USEFUL LIMITS OF DUPONT BADGE WITH AMBIENT CONDITIONS

Compound	Mean Ambient Concentration,[a] ppbv	C_A/C_{LL}[b]
Chloroform	0.088	0.80
1,2-Dichloroethane	0.52	0.074
1,1,1-Trichloroethane	1.0	1.8
Carbon Tetrachloride	0.21	1.9
Trichloroethylene	0.40	3.1
Benzene	6.0	9.2
Tetrachloroethylene	1.5	1.0
Chlorobenzene	~0.2	~0.08

(a) Reference 9, Los Angeles data.
(b) Ratio of mean ambient to lower useful limit.

REFERENCES

1. Lutz, G. Critical Literature Review of Active and Passive Air Pollution Monitors for Organic Compounds. Final Report from Battelle Columbus Laboratories to the U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. Contract No. 68-02-2686, Task 127, 1981.

2. Maze, D. T., and L. Wallace. Proceedings of the Symposium on the Development and Usage of Personal Monitors for Exposure and Health Effect Studies. EPA-600/9-79-032, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 1979.

3. 7th Annual ACGIH Topical Symposium. Dosimetry for Chemical and Physical Agents. Cincinnati, Ohio, October 6-8, 1980. (Proceedings in press.)

4. Lautenberger, W. J., E. V. Kring, and J. A. Morello. A New Personal Badge Monitor for Organic Vapors. J. Am. Ind. Hyg. Assoc., 41:737-747, 1980.

5. Gosoelink, D. W., D. L. Brown, H. G. Mullins, and S. T. Rodrigue. A New Personal Organic Vapor Monitor With In Situ Sample Elution. Paper presented at A.I.H.A. National Meeting, San Francisco, California, May 1978.

6. Tompkins, F. C., and R. L. Goldsmith. A New Personal Dosimeter for the Monitoring of Industrial Pollutants. Am. Ind. Hyg. Assoc. J., 38:371-377, 1977.

7. Nelms, L. H., K. D. Reizner, and P. W. West. Personal Vinyl Chloride Monitoring Device with Permeation Techniques for Sampling. Anal. Chem., 49(7):994-998, 1977.

8. Dommer, R. A., and R. G. Melcher. Phase Equilibrium Method for Determination of Desorption Efficiencies. Am. Ind. Hyg. Assoc. J., 39:240- , 1978.

9. Singh, H. G., L. J. Salas, A. J. Smith, and H. Shigeishi. Measurement of Potentially Hazardous Organic Chemicals in Urban Environments. Atmos. Envir., 15:601-612, 1981.